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(54) Title: PRESERVATIVE FOR GREEN FORAGE

(57) Abstract

The invention relates to a preservative for use in preparation of green forage, the preservative comprising an active ingredient which is based on formic acid and promotes lactic acid fermentation. The specificity of the lactic acid fermentation has been increased and its non-desirable side effects, such as corrosive, user and environmental hazards, have been eliminated by selecting ethyl formate as the active ingredient based on formic acid. Ethyl formate can be used as such or together with conventional active agents and auxiliary agents, such as $C_1$-$C_{10}$-carboxylic acids.

# Preservative for green forage

The invention relates to a preservative for green forage, the preservative comprising benzoic acid and an active ingredient which is based on formic acid and promotes lactic acid fermentation.

According to the AIV process, green forage can be ensiled by lowering its pH to below 4 by means of acids. The acids may be mineral acids or organic acids or their combinations.

Acidic preservative solutions cause drastic corrosion of the apparatus in which the preservative and the raw material of the silage are mixed. Also, in terms of the safety of the users, strong acid solutions are problematic, possibly causing damage to the skin and the eyes, and the acid mist produced may irritate the respiratory tract. Thus it is highly desirable to find less acidic preservatives which, nevertheless, have high preserving efficacy.

It is previously known to use ethyl formate in the storage of food as an aromatic agent or for protecting the food from detrimental spoiling. Ethyl formate is used according to US patent publication 3,062,659 to retard the sprouting of tubers and the over-ripening of fruits and vegetables. US patent publication 4,834,987 describes the use of ethyl formate in the preparation of yogurt, cheese, beer wort, and canned vegetables.

It is known to use ethyl formate as a preservative of other agricultural products such as herbs, dried fruits, legumes, grain and nuts (Pesticides 20 (12), 1986, P.P. Deo et al., "Further studies on prevention of storage molds of gram by

application of chemicals", pp. 43-44, 44, and Proceedings of an international symposium "Practical aspects of controlled atmosphere fumigation in grain storages" (1983), Perth, Western Australia, M. Muthu et al., "Ethylformate as a sage general fumigant", Central Food Technology Research Institute, Mysore 570 013, India (1984), pp. 369-393).

Furthermore, ethyl formate has been used as an insecticide for the control of the Myzus persicae aphid on packaged lettuce leaves (Journal of Economic Entomology (1984), 77 (3), pp. 569-573).

In the preparation of green forage, it is advantageous for the quality and preservation of the forage to promote lactic acid fermentation so that this fermentation is reinforced in relation to other fermentation processes and takes place at a lower temperature. It is advantageous simultaneously to inhibit adverse fermentation processes, especially to suppress the growth of those micro-organisms which decompose protein and cause butyric fermentation. Large amounts of ammonium and amines are formed in silage as the result of the decomposition of protein. Formic acid prevents the growth of protein-decomposing microbes. However, formic acid involves the above-mentioned practical problems in terms of corrosion and user safety.

It has now been observed that the said disadvantages can be eliminated and a good result can be achieved by using a preservative of a new type, which is mainly characterized in what is stated in the characterizing clause of Claim 1.

It has been realized that the preservative comprising benzoic acid and ethyl formate is superior to preservatives comprising only benzoic acid or ethyl formate.

The efficacy of ethyl formate seems to be based on the fact that, in the same manner as formic acid, it selectively promotes lactic acid fermentation. But, in contrast to the situation when formic acid is used, the pH of the forage is not lowered to below 4 by means of the preservative. When ethyl formate is used, the pH drops at a somewhat slower rate than when formic acid is added, and thereby the above-mentioned disadvantages to people and apparatus are avoided.

It is advantageous if the preservative contains ethyl formate approx. 10-98 % by weight and preferably approx. 20-80 % by weight.

When ethyl formate is thus used with benzoic acid the total quantity and concentration of it can be subtantially lowered. Benzoic acid is a preservative previously known from FI patent publication 63328, and it is known to control mold fungi in forage mixtures. However, benzoic acid and especially its salts are poorly soluble in the acid solutions, e.g. formic acid, known in ensiling. Solid state or a tendency to precipitate causes practical inconvenience of many kinds, such as nozzle clogging and sedimentation of the preservative suspension. It has now been shown surprisingly that benzoic acid and its salts dissolve well in ethyl formate, in which case these disadvantages can also be avoided.

According to one preferred embodiment, the preservative contains ethyl formate approx. 50-98 % by weight and benzoic acid approx. 2-50 % by weight.

Ethyl formate is excellently suited for preservative solutions which contain benzoic acid. The proportion of benzoic acid in the compositions may be approx. 2-50 % by weight, preferably approx. 2-25 % by weight. It is advantageous to use propionic

acid together with ethyl formate, since besides preservative properties propionic acid has a dissolving effect on benzoic acid or its salt. Formic acid can also be used in addition to or together with propionic acid.

According to one embodiment, the preservative contains ethyl formate approx. 50-70 % by weight, benzoic acid approx. 10-30 % by weight, and propionic acid or formic acid approx. 10-30 % by weight. According to another embodiment, it contains ethyl formate approx. 10-30 % by weight, benzoic acid approx. 5-20 % by weight, propionic acid approx. 25-50 % by weight, and formic acid approx. 30-60 % by weight.

The preservative according to the invention comprising benzoic acid and ethyl formate is suitable to be used for preserving green foraga, i.e. wet preserved grain, mash and green fodder.

The quantity of ethyl formate per one tonne of forage may vary within wide limits, depending on the use and on the methods of use. Likewise, the concentrations of ethyl formate may vary within wide limits in preservative compositions in which ethyl formate has been used together with other active ingredients.

Especially preferable preservative compositions contain benzoic acid or a salt thereof and ethyl formate together with formic acid and propionic acid. Preservative compositions according to the invention, containing ethyl formate, may contain, in addition to the ingredients mentioned above, also other active ingredients known per se in the ensiling of forage, such as acetic acid, hexanoic acid, heptanoic acid and octanoic acid. The said acids may be in the form of esters or salts.

The compositions according to the invention may contain besides

ethanol, propylene glycol, glycerol, urea, hexamethylene tetramine, or an emulsifier. The emulsifier may be a surface active agent, such as a nonionic active agent based on monoglyceride, and a thickening agent type polymer, such as polyvinyl alcohol, can be used as an auxiliary agent of the emulsifier or as a suspending agent.

The invention is elucidated below with examples.

Examples 1. Ethyl formate as a solvent and an active ingredient
20 parts by weight benzoic acid was dissolved into 80 parts by weight ethyl formate. A clear, stable solution, poorly miscible with water, was obtained. Its odor was not pungent, and at least in a test of short duration it did not irritate the skin as do state-of-the-art preservative solutions.

Example 2
20 parts by weight benzoic acid was dissolved in 50 parts by weight ethyl formate and 20 parts by weight propionic acid. A clear solution was obtained in which, however, a sediment formed at 3 °C. When water was added to the mixture at approx. 5-10 % of its weight, a clear solution was obtained which was stable also at the test temperature of 3 °C. With larger additions of water, a separate water phase was formed which formed an emulsion with the organic phase when stirred.

Example 3
The above example was repeated by using formic acid instead of propionic acid. A solution which was better miscible with water but was less tolerant to cooling was obtained.

Examples 4 and 5
In the laboratory, preservative solutions were prepared which contained formic acid, propionic acid and benzoic acid as ac-

tive ingredients in addition to ethyl formate. The benzoic acid was first dissolved in ethyl formate and propionic acid before the adding of the other constituents. The values are parts by weight.

Examples 6 and 7

In the manner of the previous examples, preservative solutions were prepared in which formic acid, propionic acid and benzoic acid were used as active ingredients in addition to ethyl formate. The samples were tested by defining the concentrations of lactic acid, acetic acid, and the added up ammonium and amine and the results were good.

| | Example 6 | Example 7 |
|---|---|---|
| Formic acid, 85 % | 43.5 | 57.4 |
| Propionic acid | 21.7 | 16.4 |
| Benzoic acid | 10.9 | - |
| Na benzoate | - | 8.2 |
| Ethyl formate | 21.7 | 16.4 |
| Dimodan LS* | 2.2 | 1.6 |

* Dimodan LS is a fatty acid monoglyceride

Example 8

20 g of Fusarium culmorum seed solution per 30 g of air dry grain mixture (oats, wheat, barley 1:1:1) were mixed. After 5 minutes the excess amount of the liquid was poured away. 0.12 mg and 0.24 mg of preservatives were added to the damp grains and a careful mixing was carried out. The samples were shut in an airtight vessel for 0.5 days, after which a part of the sample was poured in a Petri-bowl on two damp sheets of filter paper. The covered Petri-bowls were put in a plastic bag in a heating chamber (28 °C) for 6 days. The scale used in the assessment of the mold fungi was:

3 = fully covered by mold fungi
0 = no mold fungi at all

The preservative according to the invention contained ethyl formate and benzoic acid in the ratio 80:20, and in addition 2% by weight of $C_8$ monoglyceride.

The results as averages of three parallel experiments were the following:

| Preservative | Affected by mold fungi with a dose of 0.12 mg and 0.24 mg | |
|---|---|---|
| No preservative | (3.0) | (3.0) |
| Benzoic acid (comparison) | 1.5 | 2.0 |
| Ethyl formate (comparison) | 1.5 | 1.2 |
| Solution according to the invention | 0.8 | 0.6 |

Claims

1. A preservative for the preparation of green forage, the preservative comprising benzoic acid or a salt thereof and an active ingredient which is based on formic acid and promotes lactic acid fermentation, **characterized** in that the active ingredient based on formic acid is ethyl formate.

2. A preservative according to Claim 1, **characterized** in that it contains ethyl formate approx. 10-98% by weight, and preferably approx. 20-80 % by weight.

3. A preservative according to Claim 1 or 2, **characterized** in that it contains at least one aliphatic carboxylic acid, its derivative or its salt, having 1-10 carbon atoms in its molecule.

4. A preservative according to Claim 3, **characterized** in that the aliphatic carboxylic acid is $C_1$-$C_3$ carboxylic acid, or any mixture of the same.

5. A preservative according to any of the preceding Claims, **characterized** in that it contains ethyl formate approx. 50-98 % by weight and benzoic acid approx. 2-50 % by weight.

6. A preservative according to Claim 4, **characterized** in that it contains ethyl formate approx. 50-70 % by weight, benzoic acid approx. 10-30 % by weight, and propionic acid or formic acid approx. 10-30 % by weight.

7. A preservative according to Claim 4, **characterized** in that it contains ethyl formate approx. 10-30 % by weight, benzoic acid approx. 5-20 % by weight, propionic acid approx. 25-50 % by weight, and formic acid approx. 30-60 % by weight.

8. A preservative according to any of the above claims, **characterized** in that the weight ratio of formic acid to propionic acid is 1:10 - 10:1.

9. A preservative according to any of the above claims, **characterized** in that it contains one or more of the following auxiliary agents: ethanol, propylene glycol, glycerol, urea, hexamethylene tetramine, a surface active agent, and a thickener-type polymer.

10. A preservative according to Claim 9, **characterized** in that the surface active agent is a non-ionic active agent based on glycerol or sorbitol.

11. A preservative according to Claim 10, **characterized** in that the proportion of the surface active agent is approx. 1-5 % by weight.